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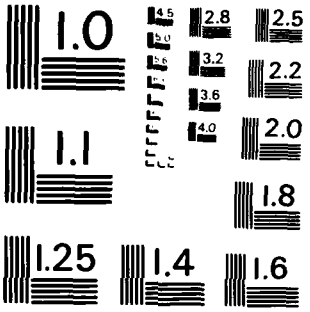

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A new process, Laser Photodeposition (based on surface photochemistry), has been demonstrated as means for localized material deposition. The spectroscopy, chemical kinetics and transport properties in adsorbate layers of metal alkyls and chlorides have been characterized. Surface-modification processes, based on reactions of monomolecular layers, have been demonstrated. The phenomenon of stimulated surface-plasma-wave scattering has been identified and shown widely important in laser/surface interactions. Applications have been demonstrated in microelectronics.

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Interaction of UV-Laser Radiation with Molecular Surface-Films

FINAL REPORT

D. J. Ehrlich and J. Y. Tsao

1 June 1984

U. S. ARMY RESEARCH OFFICE

Contract Number: MIPR ARO 120-83

Lincoln Laboratory
Massachusetts Institute of Technology

I. SUMMARY OF ACCOMPLISHMENTS

This Army Research Program has supported basic research surrounding a new laser-chemical technology for microfabrication. An emphasis has been on the physical processes occurring at solid interfaces and particularly processes occurring in chemically and physically adsorbed layers of photochemically active molecules. These adsorbate processes are critical to the new technology for spatial resolution and thin-film interface control. Prominent findings under the program are listed below. All are first-time studies in this new area of chemical physics.

1. Volatile-adlayer UV-laser reactions have been developed and applied to maskless photodeposition of metals and to in situ polymerization.
2. UV-laser surface-catalyzed reactions for photodeposition have been identified and characterized.
3. UV-laser multimolecular reactions and multiple-component reactions in adsorbates have been studied and applied to deposition of optimized metal films and catalysts by driven photochemical reactions.
4. Laser surface-modification reactions have been developed for predisposing surfaces to chemical reactions by photolysis of monolayer adsorbates. An example is the deposition of heterogeneous Natta-Ziegler catalysts.
5. A double-modulation optical reflectometric technique has been developed for thickness measurements and for spectroscopy in volatile adsorbates at submononolayer coverages.

6. The process of stimulated surface-plasma-wave scattering has been discovered and characterized on a variety of metal-film interfaces. 65-nm-period structures, the smallest by any optical technique, have been produced by VUV light scattering in germanium.
7. Studies have been made by a novel laser deposition technique of the surface diffusion of a large organometallic molecule (tetraethyl lead). Although surface diffusion of organics is of some importance, e.g., in petrochemical refining, previous techniques have been impractical for such fragile molecules.
8. The first demonstrations of optical projection patterning by microchemistry have been developed. These techniques make use of surface-modification and solid-transformation reaction. A resolution better than 0.4 μm, i.e., superior to projection lithography, has been achieved. A 0.2-μm resolution has been achieved in microchemical direct writing.

Each of these studies is the subject of several publications as listed in the attached bibliography.

The program has been cited twice during its course in the MIT president's report for its importance to microelectronics and twice in "Physics News," the annual review of the American Physical Society, for its original innovation in basic research.

II. TECHNOLOGY APPLICATIONS

The Army Research Office Program covered by this report has also developed applications in electronics in conjunction with additional support from the U.S. Department of the Air Force under a specific program sponsored by the U.S. Air Force Office of Scientific Research, and by the Defense Advanced Research Projects Agency.

A new process, laser photodeposition (based on surface photochemistry), has been demonstrated as means for localized material deposition. The spectroscopy, chemical kinetics and transport properties in adsorbate layers of metal alkyls and chlorides have been characterized. Surface-modification processes, based on reactions of monomolecular layers, have been demonstrated. The phenomenon of stimulated surface-plasma-wave scattering has been identified and shown widely important in laser/surface interactions including damage processes in high-power-laser optics. Applications have been demonstrated in fabrication of submicrometer gratings.

In FY84 several advanced applications have been developed in silicon integrated circuit technology. A specific target has been the refinement and demonstration of direct-write deposition and etching for rapid prototyping and testing functions on semicustom circuits. Aluminum and polysilicon connect/disconnect techniques, applied to commercial CMOS gate arrays, have produced working circuits and demonstrated in situ circuit modification under test conditions. This work constitutes the first demonstration of a one-step technology for "free-form" circuit routing and the first demonstration by any maskless technique on commercial circuits. There are no prefabricated switch structures and therefore there is no compromise in circuit performance

relative to the optimized commercial architecture. The same experiments have illustrated a versatile bread-boarding approach to testing of VLSI by allowing arbitrary and reversible circuit surgery for access and test of circuit substructures.

In separate work, laser photodeposition has also been applied to the problem of repair of transparent defects on fully fabricated x-ray membrane masks. No viable alternative solution has been demonstrated for this potentially fundamental problem for practical x-ray lithography. Submicrometer resolution and a compatibility with existing ion-beam technology for opaque-defect repair has been demonstrated.

In further work, the first steps have been taken in translating laser-direct-write techniques to the geometry of step-and-repeat projection lithography for large-volume production by parallel fabrication technology. Excimer-laser radiation at 193 and 157 nm, with reflective optics, have allowed printing of 0.4-μm lines by direct, single-pulse etching and doping. 0.2-μm lines in 1.5-μm-thick PMMA have been achieved by a single-pulse process in an organic bilayer.

In process-development work, a new low-temperature tungsten deposition technique has been demonstrated, a new technique for direct, patterned growth of the conducting polymer polyacetylene has also been developed (no other method exists), and a new photochemical/thermal process for rapid patterned CVD of aluminum by local surface modification has been achieved. Laser direct-writing processes for silicon deposition etching and doping have recently been extended to 0.2-μm linewidths under the program. Further details of work carried out recently under the program are given in the publications listed.